LOW TEMPERATURE SINTERABLE DIELECTRIC CERAMIC COMPOSITION, MULTILAYER CERAMIC CHIP CAPACITOR AND CERAMIC ELECTRONIC DEVICE

5   BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a dielectric ceramic composition for temperature compensation which can be sintered

10   in conjunction with an internal electrode made of a base metal at a low temperature under a reducing atmosphere, and which has a low dielectric constant and a high dielectric quality factor (Q), as well as to a multilayer ceramic chip capacitor and a ceramic electronic device each using the ceramic

15   composition.

Description of the Related Art

In recent years, with the advent of the information age, there is an increasing requirement for electronic devices which

20   increase processing speed and improve radio frequency characteristics. Multilayer ceramic chip capacitors used in, for example, high frequency circuit filters also require a low dielectric constant and a high dielectric quality factor. They are widely used as electronic devices that can provide a stable

25   reference capacitance.

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Recently, there are $(Ca,Sr)(Zr,Ti)O_3$-based, $MgO-TiO_2$-based, $BaO-TiO_2$-based, and $BaO-TiO_2-REO$-based dielectric ceramic compositions that can be used for multilayer ceramic chip capacitors. These dielectric ceramic compositions can be sintered at a high temperature of 1,200℃ or more. In this regard, in order to sinter dielectric layers made of such dielectric compositions in conjunction with internal electrodes, high melting point metals such as Palladium (Pd) and Platinum (Pt) must be used as the internal electrodes. However, Pd and Pt are more expensive and higher in resistivity, compared with base metals such as Ag and Cu. Due to higher resistivity, equivalent series resistance (ESR) and inductance (ESL) are increased at high frequency, resulting in a high dielectric loss and a low dielectric quality factor.

Therefore, in order to use base metals such as Cu as internal electrodes, the use of a dielectric ceramic composition which can be sintered at a low temperature is required. Internal electrodes made of base metals may be oxidized upon being sintered in air. Therefore, co-sintering of dielectric layers and internal electrodes must be effected in a reducing atmosphere.

Exemplary low temperature sinterable dielectric ceramic compositions are disclosed in Japanese Patent Application Laid-Open Publication No. 5-190020; U.S. Patent Nos. 5,756,408 and 4,988,651; and Japanese Patent Application Laid-Open

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Publication No. 1-102806.

Japanese Patent Application Laid-Open Publication No. 5-190020 discloses a dielectric ceramic composition that comprises a major composition represented by the general formula: $a(xBa-yCa-zSr)O-bSiO_2-cZrO_2-(d/2)Al_2O_3-eTiO_2$ (wherein $5mol\% \leq a \leq 6mol\%$, $10mol\% \leq b \leq 70mol\%$, $0mol\% < c \leq 30mol\%$, $0mol\% < d \leq 30mol\%$, $0mol\% < e \leq 30mol\%$, $a+b+c+d+e=100mol\%$; and $x+y+z=1$). The dielectric ceramic composition does not have non-reducibility and thus base metals such as Cu cannot be used as internal electrodes. Furthermore, due to the use of glass process of heating a raw material mixture to a high temperature of $1,600°C$ or more, followed by quenching quickly, it is difficult not only to disperse glass powders, but also to control particle size thereof.

U.S. Patent No. 5,756,408 discloses a glass ceramic sintered body that contains 30 to 70% by weight of (Ca,Sr)-Al-Zn-Si-O type composite oxide and 30 to 70% by weight of Ca oxide and Zr oxide or $CaZrO_3$ as a filler. Unfortunately, the dielectric quality factor of the ceramic sintered body was not considered.

U.S. Patent No. 4,988,651 discloses a dielectric ceramic composition represented by the general formula: $xBaO-ySiO_2-z\{ZrO_2(1-\beta)TiO_2(\beta 1)SnO_2(\beta 2)\}$ (wherein x, y and z are weight percentages of respective components; $x+y+z=100$; $\beta = \beta 1 + \beta 2$, $0 \leq \beta 1$, $0 \leq \beta 2$, $0.01 \leq \beta \leq 0.03$). However, due to the use of

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TiO_2, non-reducibility becomes poor.

Japanese Patent Application Laid-Open Publication No. 1-102806 discloses a dielectric ceramic composition represented by the general formula: $[x(Ba_{(1-a)}Sr_a)O-ySiO_2-zZrO_2]-Al_2O_3$. The dielectric ceramic composition can be sintered at a low temperature under a non-reducing atmosphere. However, there are disadvantages in that a temperature characteristic of capacitance is ± 100 (ppm/°C), a dielectric quality factor (Q) is 1,000, and an insulation resistance is very low in the level of 10^{12} Ω cm.

Low temperature sinterable dielectric ceramic compositions can also be used in multilayer ceramic circuit boards for electronic devices. This is because dielectric compositions for multilayer ceramic circuit boards must be sintered in conjunction with internal electrodes made of base metals with low melting point. The use of high melting point metals as internal electrodes undesirably leads to a high electric resistance. Multilayer ceramic circuit boards are used as substrates on which semiconductor elements or various electronic elements are mounted, to thereby miniaturize electronic devices.

SUMMARY OF THE INVENTION

Therefore, the present invention has been made in view

of the above problems, and it is an object of the present invention to provide a dielectric ceramic composition, which can be sintered in conjunction with an internal electrode at a low temperature under a reducing atmosphere, and which

5   satisfies a temperature characteristic of capacitance of ± 30 (ppm/℃), a low dielectric constant and a high dielectric quality factor.

Another object of the present invention is to provide a multilayer ceramic chip capacitor made of the dielectric

10   composition which can be sintered at a low temperature and has a low dielectric constant and a high dielectric quality factor at high frequency.

Yet another object of the present invention is to provide an electronic device using a multilayer ceramic

15   circuit board made of the dielectric composition which can be sintered at a low temperature and has a low dielectric constant and a high dielectric quality factor at high frequency.

In accordance with one aspect of the present invention,

20   the above and other objects can be accomplished by the provision of a dielectric ceramic composition which comprises a major composition represented by the general formula: $x\{\alpha BaO, (1-\alpha)SrO\}-y\{SiO_2\}-z\{(1-\beta)ZrO_2, \beta Al_2O_3\}$ (wherein x, y and z are weight percentages; x+y+z=100, $55 \leq x \leq 75$, $10 \leq y \leq 35$, and $5 \leq z \leq 30$,

25   α and β are moles; $0.4 \leq \alpha \leq 0.8$ and $0.01 \leq \beta \leq 0.07$) and 2 to 10

parts by weight of a Zn-B-silicate glass composition, per 100 parts by weight of the major composition.

Preferably, the Zn-B-silicate glass composition for the dielectric composition of the present invention comprises 15 to 25% by weight of SiO_2, 20 to 30% by weight of B_2O_3, and 40 to 50% by weight of ZnO. It further comprises 7% by weight or less of at least one selected from alkaline metals such as Li, K and Na, and 5% by weight or less of Al_2O_3.

In accordance with another aspect of the present invention, there is provided a multilayer ceramic chip capacitor comprising a plurality of dielectric ceramic layers, internal electrodes arrayed inside the dielectric ceramic layers, and outer electrodes electrically connected to the internal electrodes, characterized in that the dielectric ceramic layer is a sintered body of the dielectric ceramic composition which comprises a major composition represented by the general formula: $x\{\alpha BaO, (1-\alpha)SrO\}-y\{SiO_2\}-z\{(1-\beta)ZrO_2, \beta Al_2O_3\}$ (wherein x, y and z are weight percentages; x+y+z=100, $55 \leq x \leq 75$, $10 \leq y \leq 35$, and $5 \leq z \leq 30$, α and β are moles; $0.4 \leq \alpha \leq 0.8$ and $0.01 \leq \beta \leq 0.07$) and 2 to 10 parts by weight of a Zn-B-silicate glass composition, per 100 parts by weight of the major composition, and the internal electrode is made of a conductive base metal material.

In accordance with yet another aspect of the present invention, there is provided a ceramic electronic device

comprising a multilayer ceramic circuit board and at least one electronic elements which are mounted on the multilayer ceramic circuit board, characterized in that the multilayer ceramic circuit board comprises a plurality of dielectric ceramic layers, internal electrodes arrayed inside the dielectric ceramic layers, and outer electrodes electrically connected to the internal electrodes, the dielectric ceramic layer is a sintered body of the dielectric ceramic composition which comprises a major composition represented by the general formula: $x\{\alpha\ BaO,\ (1-\alpha)SrO\}-y\{SiO_2\}-z\{(1-\beta)ZrO_2,\ \beta\ Al_2O_3\}$ (wherein x, y and z are weight percentages; $x+y+z=100$, $55\leq x\leq 75$, $10\leq y\leq 35$, and $5\leq z\leq 30$, α and β are moles; $0.4\leq \alpha \leq 0.8$, and $0.01\leq \beta \leq 0.07$) and 2 to 10 parts by weight of a Zn-B-silicate glass composition, per 100 parts by weight of the major composition, and the internal electrode is made of a conductive base metal material.

BRIEF DESCRIPTION OF THE DRAWINGS

The above and other objects, features and other advantages of the present invention will be more clearly understood from the following detailed description taken in conjunction with the accompanying drawing, in which:

Fig. 1 is a triangular diagram showing compositional proportions of $\{BaO+SrO\}$, $\{SiO_2\}$ and $\{ZrO_2+Al_2O_3\}$;

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Fig. 2 is a view showing one embodiment of a multilayer ceramic chip capacitor; and

Fig. 3 is a view showing one embodiment of an electronic device.

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DESCRIPTION OF THE PREFERRED EMBODIMENTS

Hereinafter, the present invention will be described in more detail.

10   The dielectric composition of the present invention has a temperature characteristic of capacitance of ± 30 (ppm/°C), a dielectric quality factor (Q) of 2,000 or more, an insulation resistance of 1×10^{13} Ω cm or more, and a dielectric constant of 13 or less. Furthermore, it can be sintered in conjunction with

15   an internal electrode made of a base metal at a low temperature of 1,000°C or less due to its non-reducibility. Therefore, it is suitable for use in preparing a multilayer ceramic chip capacitor and a multilayer ceramic circuit board for an electronic device, requiring a low melting point base metal for

20   an internal electrode.

Described below is the dielectric ceramic composition of the present invention.

Fig. 1 is a triangular diagram showing compositional

25   proportions of {BaO+SrO}, {SiO$_2$} and {ZrO$_2$+Al$_2$O$_3$}. The numbers

on the drawing indicate multilayer ceramic chip capacitor samples listed in Table 2 as will be described hereinafter. The major composition of the present invention represented by the general formula: $x\{\alpha BaO, (1-\alpha)SrO\}-y\{SiO_2\}-z\{(1-\beta)ZrO_2, \beta Al_2O_3\}$ falls within the polygonal area defined by the points A(x=75wt%, y=20wt%, z=5wt%), B(x=75wt%, y=10wt%, z=25wt%), C(x=60wt%, y=10wt%, z=30wt%), D(x=55wt%, y=15wt%, z=30wt%), E(x=55wt%, y=35wt%, z=10wt%) and F(x=60wt%, y=35wt%, z=5wt%).

$\{\alpha BaO, (1-\alpha)SrO\}$: 55 to 75% by weight ($\alpha$ is mole; $0.4\leq \alpha \leq 0.8$)

If the content of $\{\alpha BaO, (1-\alpha)SrO\}$ is less than 55% by weight, a dielectric quality factor (Q) is lowered and a temperature characteristic of capacitance is outside the range of ± 30 (ppm/℃). On the other hand, if it exceeds 75% by weight, all electric properties including a dielectric constant, a dielectric quality factor (Q), a temperature characteristic of capacitance and resistivity are poor. As the content of $\{\alpha BaO, (1-\alpha)SrO\}$ is larger, a temperature characteristic of capacitance increases in a negative direction, while as the content of $\{\alpha BaO, (1-\alpha)SrO\}$ is smaller, a temperature characteristic of capacitance increases in a positive direction. It is most preferable to limit the content of $\{\alpha BaO, (1-\alpha)SrO\}$ to a range of 60 to 65% by weight.

It is preferable to limit the α value to a range of 0.4 to

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0.8. As the α value is larger, a temperature characteristic of capacitance increases in a negative direction. On the other hand, as the α value is smaller, a temperature characteristic of capacitance increases in a positive direction. If the α value is outside the above range, a temperature characteristic of capacitance is outside the range of ± 30 (ppm/°C).

SiO$_2$: 10 to 35% by weight

If the content of SiO$_2$ exceeds 35% by weight, a dielectric quality factor is less than 1,000 and a temperature characteristic of capacitance is outside the range of ± 30 (ppm/°C). If the content of SiO$_2$ is larger, a temperature characteristic of capacitance increases in a positive direction, while if it is smaller, a temperature characteristic of capacitance increases in a negative direction. If the content of SiO$_2$ is less than 10% by weight, a dielectric quality factor (Q), a temperature characteristic of capacitance, and resistivity are poor. It is most preferable to limit the content of SiO$_2$ to a range of 20 to 25% by weight.

{(1-β)ZrO$_2$, β Al$_2$O$_3$}: 5 to 30% by weight (β is mole; 0.01$\le \beta \le$ 0.07)

If the content of {(1-β)ZrO$_2$, β Al$_2$O$_3$} is outside the above range, a dielectric quality factor (Q) is less than 1,500 and a temperature characteristic of capacitance is outside the

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range of ± 30 (ppm/℃). If the content of {(1-β)ZrO₂, β Al₂O₃} is larger, a temperature characteristic of capacitance increases in a positive direction, while if it is smaller, a temperature characteristic of capacitance increases in a negative direction. It is most preferable to limit the content of {(1-β)ZrO₂, β Al₂O₃} to a range of 10 to 20% by weight.

If the β value is outside the above range, a temperature characteristic of capacitance is outside the range of ± 30 (ppm/℃). If the β value is larger, a temperature characteristic of capacitance increases in a positive direction and resistivity is less than 1.0×10^{12} Ω cm due to formation of glass phase on the surfaces of sintered dielectric bodies. On the other hand, if the β value is smaller, a temperature characteristic of capacitance increases in a negative direction and dense sintered dielectric bodies cannot be obtained, resulting in a dielectric quality factor (Q) of less than 1,000.

In accordance with the present invention, a Zn-B-silicate glass composition is added to the major composition that falls within the polygonal area defined by the points A, B, C, D, E and F in Fig. 1. If the major composition is the one having a set of x, y and z falling in the area outside the side ABC in Fig. 1, regardless of the added amount of the glass composition, glass phase on the surfaces of sintered dielectric bodies is present, resulting in less than 1.0×10^{12} Ω cm of

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resistivity.   Furthermore,   a   temperature   characteristic   of
capacitance is outside the range of ± 30 (ppm/°C) and formation
of electrodes is difficult.

5   Zn-B-silicate glass composition: 2 to 10 parts by weight
based on 100 parts by weight of the major composition

Preferably, the Zn-B-silicate glass composition of the
present invention comprises SiO_2, B_2O_3 and ZnO.   Such glass
components react with Al_2O_3 of the major composition when

10   sintered at a temperature of 800 to 1,000°C, resulting in
crystallization of some glass composition. Such crystallization
improves   the   mechanical   stress   of   dielectric   layers.
Preferably, the Zn-B-silicate glass composition comprises 15 to
25% by weight of SiO_2, 20 to 30% by weight of B_2O_3 and 40 to 50%

15   by weight of ZnO.   The SiO_2 content of less than 15% by weight
may cause crystallization of all the glass composition, making
it difficult to lower a sintering temperature.   On the other
hand, the SiO_2 content of more than 25% by weight may raise the
melting   point   of   the   glass   composition,   and   thus   low

20   temperature sintering is difficult.   If the content of B_2O_3 is
less than 20% by weight or the content of ZnO is less than 40%
by weight, the melting point of the glass composition is
increased, whereby low temperature sintering is difficult.   On
the other hand, if the content of B_2O_3 exceeds 30% by weight or

25   the content of ZnO exceeds 50% by weight, crystallization of

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all the glass composition is caused, making it difficult to lower a sintering temperature. Preferably, the glass composition further comprises 7% by weight or less of at least one selected from alkaline metals such as Li, K and Na, and 5% by weight or less of Al_2O_3. Alkaline metals act to lower a sintering temperature. In this regard, if the content of the alkaline metals exceeds 7% by weight, the dielectric composition forms dielectric layers of glass phase and thus sintered bodies cannot be obtained. Al_2O_3 acts to facilitate the formation of glass phase. In this regard, the content of Al_2O_3 of more than 5% by weight may retard the formation of glass phase. One embodiment of the Zn-B-silicate glass composition is presented in Table 1 below.

Table 1

Glass composition (% by weight)					
Al_2O_3	SiO_2	ZnO	B_2O_3	Alkaline metals	Others
<5	15-25	40-50	20-30	Li<5, K<5	Ce<2, Sn<2

Preferably, the content of the Zn-B-silicate glass composition of the present invention is 2 to 10 parts by weight based on 100 parts by weight of the major composition. If the content of the glass composition is outside this range, a temperature characteristic of capacitance is outside the range

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of $\pm$ 30(ppm/℃).   In detail, as the content of the glass
composition   is   larger,   a   temperature   characteristic   of
capacitance increases in a positive direction.   Also, there is
formation of glass phase on the surface of sintered dielectric

5   bodies, resulting in less than 1.0×10^{12} Ω cm of resistivity.   On
the other hand, as the content of the glass composition is
smaller, a temperature characteristic of capacitance increases
in a negative direction.   Also, dense sintered bodies cannot be
obtained and low temperature sintering cannot be accomplished.

10   Most preferably, the content of the glass composition of the
present invention is 4 to 8 parts by weight based on 100 parts
by weight of the major composition.

The   dielectric   composition   of   the   present   invention
satisfies a temperature characteristic of capacitance of $\pm$ 30

15   (ppm/℃), a dielectric quality factor (Q) of 2,000 or more, an
insulation resistance of 1×10^{13} Ω cm or more, and a dielectric
constant of 13 or less.   It can also be sintered in conjunction
with an internal electrode made of a base metal at a low
temperature of 1,000℃ or less under a neutral or reducing

20   atmosphere and exhibits a high dielectric quality factor at
high frequency (100 MHz or more).   Therefore, it can be used in
preparing a multilayer ceramic chip capacitor and a multilayer
ceramic circuit board for an electronic device, requiring a
small size, light weight and thin thickness.

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Next, the multilayer ceramic chip capacitor of the present invention will be described.

The dielectric composition of the present invention can be sintered in conjunction with an internal electrode made of a low melting point base metal under a neutral or reducing atmosphere and it satisfies a temperature characteristic of capacitance of ± 30 (ppm/℃), a dielectric quality factor (Q) of 2,000 or more, an insulation resistance of 1×10^{13} Ω cm or more, and a dielectric constant of 13 or less. Therefore, it can be used in preparing a multilayer ceramic chip capacitor requiring the electric properties mentioned above.

Fig. 2 is a view showing one embodiment of a multilayer ceramic chip capacitor. The multilayer ceramic chip capacitor comprises a plurality of dielectric ceramic layers 13, internal electrodes 15 arrayed inside the dielectric ceramic layers 13, and outer electrodes 17 electrically connected to the internal electrodes 15.

In accordance with the present invention, the dielectric ceramic layer is a sintered body of the dielectric ceramic composition which comprises a major composition represented by the general formula: $x\{\alpha \, BaO, \; (1-\alpha) \, SrO\} - y\{SiO_2\} - z\{(1-\beta) \, ZrO_2, \; \beta \, Al_2O_3\}$ (wherein x, y and z are weight percentages; x+y+z=100, $55 \leq x \leq 75$, $10 \leq y \leq 35$, and $5 \leq z \leq 30$, α and β are moles; $0.4 \leq \alpha \leq 0.8$, and $0.01 \leq \beta \leq 0.07$) and 2 to 10 parts by weight of a Zn-B-silicate glass composition, per 100 parts by weight of

the major composition.

The internal electrode is made of a conductive base metal material such as Cu, Ag, Ni and alloys thereof. The external electrodes are composed of sintered layers of a conductive metal powder supplemented with a glass frit. A plating layer can be formed thereon. The plating layer is comprised of Ni, Cu or Ni-Cu alloys or a second plating layer containing tin or solder can be formed thereon.

One method for preparing the multilayer ceramic chip capacitor of the present invention is as follows. First, starting materials for the dielectric ceramic composition of the present invention are prepared in the form of powders by a solid phase method whereby oxides or carbonates are calcined at a high temperature, or a wet synthesis method such as a hydrothermal synthesis method and an alkoxide method. The prepared major composition powders and glass powders are mixed in a prescribed composition ratio. The mixed powders are turned into slurry by addition of an organic binder. In this case, it is preferable to limit the mean particle size of the major composition powder to a range of 0.3 to 1 μm. If the particle size is outside this range, an undesirable second phase is formed or unreacted raw material powders are left.

The slurry is molded into a sheet. Inner electrodes made of conductive base metals are then formed on one face of the sheet. Any methods including screen printing, vacuum deposition

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and plating may be used for forming the inner electrodes. Then, a required number of the sheets having the inner electrodes are laminated, to form a laminated body after pressing. The laminated body is sintered at a predetermined temperature under

5   a reducing atmosphere. In accordance with the present invention, the sintering is accomplished at 1,000°C or less. The sintering may be carried out under a neutral or reducing atmosphere of a low oxygen partial pressure state, i.e. a hydrogen partial pressure represented by the formula: {Log

10   (PH_2/PH_2O)} is -2 to -4. If the hydrogen partial pressure is more than -2, binder carbon remains un-oxidized and thus internal defects of sintered bodies may be caused. As a result, an insulation resistance may be lowered or internal cracks may be formed. If the hydrogen partial pressure is less than -4,

15   internal electrodes may be oxidized within the range of the sintering temperature.

A pair of outer electrodes is formed on both side ends of the laminated body so as to be electrically connected to the inner electrodes, thereby completing the multilayer ceramic

20   chip capacitor. Alternatively, the outer electrodes may be applied to the laminated body before sintering. Plating layers may be formed, if necessary, on the outer electrodes.

Finally, the electronic device of the present invention

25   will be described.

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The dielectric composition of the present invention can be sintered in conjunction with an internal electrode made of a low melting point base metal under a reducing atmosphere and it satisfies a temperature characteristic of capacitance of ± 30 (ppm/$°C$), a dielectric quality factor (Q) of 2,000 or more, an insulation resistance of 1×10^{13} Ω cm or more, and a dielectric constant of 13 or less. Therefore, it can be used in preparing a multilayer ceramic circuit board for an electronic device requiring the electric properties mentioned above.

Fig. 3 is a view showing one embodiment of an electronic device. The ceramic electronic device comprises a multilayer ceramic circuit board 2 and at least one electronic elements 8 which are mounted on the multilayer ceramic circuit board 2 and which constitute a circuit along with a plurality of internal electrodes 5. The multilayer ceramic circuit board comprises a plurality of dielectric ceramic layers, internal electrodes arrayed inside the dielectric ceramic layers, and outer electrodes 7 electrically connected to the internal electrodes.

In accordance with the present invention, the dielectric ceramic layer for the multilayer ceramic circuit board is a sintered body of the dielectric ceramic composition which comprises a major composition represented by the general formula: $x\{\alpha\ BaO,\ (1-\alpha)SrO\}-y\{SiO_2\}-z\{(1-\beta)ZrO_2,\ \beta\ Al_2O_3\}$ (wherein x, y and z are weight percentages; x+y+z=100,

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$55 \leq x \leq 75$, $10 \leq y \leq 35$, and $5 \leq z \leq 30$, α and β are moles; $0.4 \leq \alpha \leq 0.8$, and $0.01 \leq \beta \leq 0.07$) and 2 to 10 parts by weight of a Zn-B-silicate glass composition, per 100 parts by weight of the major composition.

5   The internal electrode is made of a conductive base metal material such as Cu, Ag, Ni and alloys thereof.

The internal electrodes 5 used for the multilayer ceramic circuit board of the present invention may be used to prepare a multilayer ceramic chip capacitor, along with at least one part of the dielectric ceramic layers 3.

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The multilayer ceramic circuit board of the present invention may be used as substrate for multi-chip modules, hybrid ICs and the like. Various electronic elements are mounted on the multilayer ceramic circuit board to thereby form an electronic device. A representative electronic device

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is LTCC (Low Temperature Cofirable Ceramic).

Hereinafter, the present invention will be described in more detail by way of the following non-limiting examples.

20   Examples

$BaCO_3$, $SrCO_3$, ZrO_2, Al_2O_3 and SiO_2 with purity of 99% or more as starting ceramic materials were weighed and completely mixed with a ball mill, to thereby obtain slurry. The slurry was dried without occurrence of layer separation to yield

25   ceramic powder mixture of a mean particle size of 0.3 to 1.0 μm.

Then, the ceramic powders were calcined for 1 hour to 4 hours at 750℃ to 950℃.

Each component of a Zn-B-silicate glass composition was wet milled into a glass composition powder mixture with a particle size of 0.3 to 1.0 μm with a zirconia ball using water or ethanol. The glass composition was composed of 20.57% by weight of SiO_2, 22.94% by weight of B_2O_3, 43.93% by weight of ZnO, 3.04% by weight of Li_2O, 3.30% by weight of K_2O, 3.95% by weight of Al_2O_3, and other impurities.

The ceramic powders and glass powders were mixed to thereby make slurry. The slurry was transformed into a sheet with a thickness of 15 to 70 μm by a die caster. Internal electrodes made of Cu were printed on the transformed sheet and then 3 to 10 layers of the pattern printed sheets were laminated one onto another. The resultant laminates were cut and sintered under a low oxygen partial pressure (N_2-H_2 gas atmosphere), i.e. $Log(PH_2/PH_2O)$: -2 to -4. The sintering was carried out for 1 hour to 4 hours at temperatures listed in Table 2 below to thereby form plate-shaped sintered bodies of 10mm x 10mm x 0.5mm.

In-Ga alloys were applied on the both end faces of the sintered bodies to form external electrodes in order to obtain multilayer ceramic chip capacitor samples. The sample capacitors prepared as the above were evaluated for electric properties such as electric constant (K), dielectric quality

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factor (Q), temperature characteristic of capacitance (TCC), and resistivity (Ω cm).

Dielectric constant (K) and dielectric quality factor (Q)

5 were measured at 1 MHz, 1Vrms, 25℃ using HP4278A.

Temperature characteristic of capacitance was evaluated using the standard capacitance at 25℃ (C_{25}), the capacitance at -55℃ (C_{-55}), and the capacitance at 125℃ (C_{125}), using the following equation:

10 TCC (ppm/℃)= {(C_T-C_{25})/C_{25}(T-25℃)} x 10^6 (wherein C_T is capacitance at T).

Resistivity (ρ 25) was evaluated in Ω cm unit using a measured leakage current after applying a DC voltage of 250V for 60 seconds at 25℃.

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Table 2

Sample	Major composition					Glass	Sintering temp. (℃)	Electric property			
	$x\{\alpha \text{ BaO}, (1-\alpha)\text{SrO}\}$		$y\{\text{SiO}_2\}$	$Z\{(1-\beta)\text{ZrO}_2, \beta \text{Al}_2\text{O}_3\}$				Dielectric constant (K, 25℃)	Q (25℃)	TCC (ppm/℃)	Resistivity (Ω cm)
	α	x	y	z	β						
1	0.6	75	20	5	0.01	4	990	13	2250	−20	2.9×10^{14}
2	0.6	75	10	15	0.01	4	1000	13	2120	−30	4.2×10^{14}
3	0.6	65	20	15	0.02	4	970	12	2450	−20	2.2×10^{14}
4	0.6	55	20	25	0.02	4	950	11	2530	+20	1.1×10^{14}
5	0.6	55	30	15	0.02	4	930	11	2300	+30	1.6×10^{14}
6	0.6	65	30	5	0.03	4	950	12	2420	0	2.6×10^{14}
7	0.6	80	12.5	7.5	0.03	4	1050	14	540	−150	8.2×10^{11}
8	0.6	72.5	5	22.5	0.03	4	1100	13	840	−120	1.1×10^{11}
9	0.6	55	10	35	0.03	4	970	11	520	+90	4.0×10^{11}
10	0.6	50	27.5	22.5	0.03	4	910	11	1220	+150	1.0×10^{11}
11	0.6	55	40	5	0.04	4	890	11	660	+60	2.7×10^{11}
12	0.6	71.3	26	2.7	0.04	8	950	13	820	−60	8.6×10^{11}
13	0.5	70	20	10	0.04	8	950	12	2620	−20	1.7×10^{14}
14	0.5	70	10	20	0.04	8	970	12	2350	0	1.6×10^{13}
15	0.5	60	20	20	0.04	8	950	12	2940	+20	4.9×10^{13}

x, y and z are weight percentages.

The content of glass is based on 100 parts by weight of major composition

Table 2 (continued)

Sample	Major composition					Glass	Sintering temp. (°C)	Electric property			
	$x\{\alpha\,BaO,\,(1-\alpha)SrO\}$		$y\{SiO_2\}$	$z\{(1-\beta)ZrO_2,\,\beta\,Al_2O_3\}$				Dielectric constant (K,25°C)	Q (25°C)	TCC (ppm/°C)	Resistivity (Ω cm)
	α	x	y	z	β						
16	0.5	60	30	10	0.05	8	930	11	3200	+10	3.4×10^{13}
17	0.8	70	17.5	12.5	0.05	8	970	12	3420	−10	1.7×10^{13}
18	0.8	65	15	20	0.05	8	950	12	3620	0	4.7×10^{13}
19	0.8	60	22.5	17.5	0.05	8	950	11	3240	+10	2.7×10^{13}
20	0.8	65	25	10	0.05	8	950	12	2920	+10	1.3×10^{13}
21	0.8	65	20	15	0.06	8	970	12	4120	+10	4.5×10^{13}
22	0.3	70	10	20	0.06	8	970	11	2250	+60	1.9×10^{13}
23	0.7	60	20	20	0.06	8	950	11	2640	0	2.4×10^{13}
24	0.9	60	30	10	0.06	8	950	13	2850	−90	3.1×10^{13}
25	0.7	75	20	5	0	8	1030	14	640	−60	1.8×10^{12}
26	0.7	65	20	15	0.04	8	950	12	2630	−20	1.3×10^{13}
27	0.7	55	30	15	0.08	8	910	11	1260	+90	1.7×10^{11}
28	0.7	70	17.5	12.5	0.07	1	1050	14	3520	−150	2.4×10^{14}
29	0.7	65	15	20	0.07	4	970	12	2850	−10	3.0×10^{14}
30	0.7	60	22.5	17.5	0.07	8	950	11	2420	+20	1.2×10^{13}
31	0.7	65	25	10	0.07	11	930	12	320	+90	1.3×10^{11}

x, y and z are weight percentages.

The content of glass is based on 100 parts by weight of major composition

As shown in Table 2, the capacitor of sample 7, in which

the content of {BaO+SrO} exceeded 75% by weight, exhibited a high dielectric constant of 14 and a low dielectric quality factor (Q) of less than 1,000. The capacitor of sample 10, in which the content of {BaO+SrO} was less than 55% by weight,

5   exhibited a dielectric quality factor (Q) of less than 1,500 and a temperature characteristic of capacitance outside the range of ± 30 (ppm/℃).

In case of the capacitor of sample 11, in which the content of SiO_2 exceeded 35% by weight, a dielectric quality

10   factor (Q) was less than 1,000 and a temperature characteristic of capacitance was outside the range of ± 30 (ppm/℃).

In case of the capacitors of samples 9 and 12, in which the content of {ZrO_2+Al_2O_3} was outside the range, a dielectric quality factor (Q) was less than 1,500 and a temperature

15   characteristic of capacitance was outside the range of ± 30 (ppm/℃).

In case of the capacitors of samples 22 and 24, in which the α value was outside the range, a temperature characteristic of capacitance was outside the range of ± 30 (ppm/℃).

20   In case of the capacitors of samples 25 and 27, in which the β value was outside the range, a temperature characteristic of capacitance was outside the range of ± 30 (ppm/℃). The capacitor of sample 25 did not have dense sintered bodies and thus exhibited a dielectric quality factor (Q) of less than

25   1,000. The capacitor of sample 27 exhibited resistivity of less

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than 1.0×10^{12} Ω cm due to formation of glass phase on the surfaces of sintered dielectric bodies.

In case of the capacitors of samples 28 and 31, in which the content of Zn-B-silicate glass composition was outside the range, a temperature characteristic of capacitance was outside the range of ± 30 (ppm/℃). In case of the capacitor of sample 28, a dense sintered body was not obtained and a sintering temperature was as high as 1,050℃. The capacitor of sample 31 exhibited resistivity of less than 1.0×10^{12} Ω cm due to formation of glass phase on the surface of sintered dielectric bodies.

As apparent from the above description, the dielectric composition of the present invention can be sintered in conjunction with an internal electrode made of a low melting point base metal at a low temperature of 1,000℃ or less. Furthermore, it satisfies a temperature characteristic of capacitance of ± 30(ppm/℃), a dielectric quality factor (Q) of 2,000 or more, an insulation resistance at 25℃ of 1×10^{13} Ω cm or more, and a dielectric constant of 13 or less. Therefore, it is suitable for use in preparing a multilayer ceramic chip capacitor and a multilayer ceramic circuit board for an electronic device requiring the electric properties mentioned above.

Although the preferred embodiments of the present invention have been disclosed for illustrative purposes, those

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skilled in the art will appreciate that various modifications, additions and substitutions are possible, without departing from the scope and spirit of the invention as disclosed in the accompanying claims.

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